UDC 666.232.6:66.015.4

PRODUCTION OF INITIAL COMPOUNDS FOR SPINELLIDE CERAMICS BY THE CHEMICAL PRECIPITATION METHOD

N. M. Bobkova,[1] E. V. Radion,[1] and A. E. Sokolovskii[1]

Translated from Steklo i Keramika, No. 9, pp. 16 – 17, September, 2002.

The processes of synthesis of initial compounds for magnesium spinel in chemical precipitation are studied. It is established that the choice of initial salts (nitrates, chlorides, sulfates) has virtually no effect on the phase composition of heat-treated products; however, it has a significant effect on the properties of the initial precipitates.

The development of scientific principles of formation and regulation of structures and phase states of high-melting compounds with good physicomechanical parameters is one of the purposes of the contemporary science of materials. This is linked to prioritized directions of engineering based on new progressive technologies requiring materials that can operate in extreme conditions.

A new direction of technological upgrade is the use of fine chemical synthesis based on the chemical preciptation method. This method is especially convenient in synthesis of extremely high-melting compounds, which include some practically important compounds of the spinel type.

Of all various spinels ($Me^{2+}Me^{3+}O_4$), the one most commonly used is aluminomagnesium spinel $MgAl_2O_4$, whose melting point is 2135°C and whose TCLE is $59.3 \times 10^{-7}\ K^{-1}$.

Articles based on sintered spinel are produced by a two-stage technology. The spinel is synthesized by firing a briquette (sinter) of finely disperse MgO and Al_2O_3 at a temperature of 1300 – 1400°C (with an organic binder). The initial materials, i.e., MgO and Al_2O_3, in turn, are produced from magnesite ore $MgCO_3$ and aluminum hydroxide by calcination. After crushing and milling of spinel briquettes, the resulting powder is used to produce articles using a nonplastic technology. The firing temperature is 1750°C.

It appears impossible to produce articles using a one-stage technology, since the synthesis of spinel is accompanied by temperature expansion (linear 7 – 8% and volume 22 – 24%) caused by the lower density of spinel ($3.58 \times 10^3\ kg/m^3$) compared to the density of alumina ($3.99 \times 10^3\ kg/m^3$). Maximum expansion is observed in the temperature range 1200 – 1300°C coinciding with the end of spinel formation. However, it is difficult to obtain dense spinel-based ceramics, although numerous attempts have been made using mineralizers, spray pyrolysis, or thermal treatment of polycrystalline samples made of mixture of oxides [1, 2]. Therefore, production of spinel using the method of fine chemical synthesis methods was researched as well.

All literary data on methods for producing initial materials for synthesis of spinel from solutions can be split into three main groups:

– methods using coprecipitation of the components;

– methods in which oxide of the first component is impregnated with an aqueous solution of salt of the second component (the impregnation method);

– methods of consecutive accretion of hydroxide of the first component on the carrier hydroxide of the second component.

It is known that the method of coprecipitation from concentrated solutions makes it possible to increase the reaction capacity of chemical agents [3, 4]. This has been tested on aqueous solutions of magnesium and aluminum sulfates, chlorides and nitrates, as well as magnesium and aluminum hydroxides. The temperature of synthesis of spinel in this case decreases by 200 – 300°C.

The authors in [5] developed a new method for coprecipitation of active powder for the synthesis of noble spinel, which consists of joint precipitation of magnesium and aluminum hydroxides from solutions of sodium metaaluminate $NaAlO_2$ and magnesium salt, for instance, $MgSO_4$. The latter can be replaced by base magnesium carbonate $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$. It is possible to use $NaAlO_2$ instead of aluminum salts. Two-hour sintering at 1730°C of briquettes molded from the powder produced by the above described coprecipitation method and preliminarily calcined at 900°C makes it possible to synthesize spinel with a relative density of 0.9, i.e., this is one of the best currently known products.

Despite a number of publications dedicated to chemical methods of spinel synthesis, data on the properties of materials based on such spinel are missing. Furthermore, in most

[1] Belarus State Technological University, Minsk, Belarus.

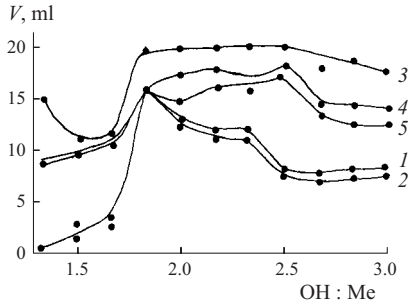

Fig. 1. Apparent volume V of precipitate versus the ratio OH : Me for chloride (*1*, *2*) and sulfate (*3* – *5*) solutions. Duration of aging: *1*, *2*, *3*, *4*, and *5*) 2, 5, 3, 2, and 4 days, respectively.

cases the sintering temperatures of the end product that are used are unjustifiably high (≥ 1700°C), which prevents estimating the efficiency of the chemical precipitation methods.

The present study describes the results of chemical precipitation using magnesium and aluminum nitrates, sulfates, and chlorides and the properties of these precipitates.

To determine the conditions for producing dense precipitate that is the most technologically acceptable, its apparent volume was determined in experiments. The type of the anion varied from chloride to sulfate, the quantity of the precipitator, i.e., the ratio of OH : Me, varied from 1.25 to 3.25, and the aging duration varied from 15 min to 5 days.

Settling of the precipitate virtually stopped after 30 – 40 min. The dependence of the apparent volume of the precipitate on the OH : Me ratio and the aging duration is indicated in Fig. 1. It can be seen that, all other terms being equal, precipitates from chloride solutions are denser and have a lower volume. The aging duration has little effect on the volume of these precipitates. The apparent volume of the precipitate from sulfate solutions gradually decreases during 4 days of aging; however, even then it is nearly twice that of the chloride precipitate. The latter is the most technologically suitable: it is dense, has a minimum volume, settles quickly, and can be easily filtered.

The study of the precipitates by the DTA methods (a Q-1500D derivatograph) within the temperature interval of 20 – 1000°C and the heating rate of 10 K/min established that, according to the endothermic effect, the main water loss occurs in several stages at temperatures of 120 – 140, 260 – 265, and 375 – 460°C. The weight loss of the precipitate synthesized under the optimum conditions is 41.07 – 43.57%. This is nearly half the weight loss of similarly prepared samples [3]. Furthermore, the weight loss process ends at a slightly lower temperature, especially in nitrate-based precipitates: at 865°C instead of 1000 – 1100°C.

According to the data in [6], decomposition of aluminum hydroxide produced by precipitation either by ammonia solution or by sodium hydroxide solution is accompanied by an endothermic effect with the minimum at the temperature of 160°C. An exothermic effect caused by crystallization of γ-Al_2O_3 is observed at a temperature of 380°C. Since such effects were not observed in our case, we may conclude that aluminum (III) and magnesium (II) in precipitation react and form a new compound different from aluminum hydroxide.

In order to obtain IR spectra, precipitates obtained from nitrates, chlorides, and sulfates were washed from impurities and dried in a drying cabinet for 10 h at a temperature of 100°C. The spectra were taken using a Specord M80 instrument. All spectra exhibit bands due to the valence vibrations of molecular water and hydroxyl groups in the range of 2800 – 3700 cm^{-1}. The blurred appearance of this band points to a substantial content of non-structural water in all samples. The absorption bands caused by the deformation vibrations of H_2O molecules (1615 – 1640 cm^{-1}) are significantly less intense. The narrow absorption bands in the range of 1387 and 1020 cm^{-1} are most probably due to the deformation vibrations of hydroxyl groups.

A number of absorption bands are observed in the range of 450 – 700 cm^{-1}, which can be generated either by the valence vibrations of Me – O bonds, or by the libration vibrations of crystallization water [7].

To determine the possibility of using the obtained precipitates as precursors for spinel production, they were subjected to heat treatment. Hydroxide precipitates were washed from impurity ions, dried in a drying cabinet at a temperature of 100°C, and then subjected to preliminary heat treatment at 900°C to remove water. Next, they were heat-treated at 1250°C for 1 h. An analysis of the x-ray patterns of the heat-treated products indicated that the main and only phase in all calcined samples was aluminomagnesium spinel $MgO \cdot Al_2O_3$. Only the diffraction patterns of samples obtained from sulfates exhibit a weak reflection corresponding to periclase.

Thus, the selection of initial salts (nitrates, chlorides, sulfates) has virtually no effect on the phase composition of the heat-treated products; however, it has a significant effect on the properties of initial precipitates.

REFERENCES

1. K. Hamano, Z. Hakagawa, and M. Sakaguchi, "Effect of MgO/Al_2O_3 ratio on sintering of spinel ceramics," *Rep. Res. Lab. Eng. Mater. Tokyo Inst. Technol.*, **50**(9), 101 – 111 (1984).
2. N. A. Toropov and N. A. Sirazhiddinov, "The effect of rare-earth element oxides on the kinetics of formation of magnesium aluminate in the solid phase," *Uzb. Khim. Zh.*, No. 5, 38 – 42 (1963).
3. T. Yu. Chemekova and O. L. Filippova, "The effect of conditions of synthesis on the parameters of sintering of spinel-based ceramics," *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **26**(3), 656 – 657 (1990).
4. T. S. Witkowski and J. B. Munro, "Coprecipitated spinel for refractory applications," *Refract. J.*, **64**, 437 – 442 (1989).
5. N. Burtan and S. Vlaicu, "Spinellpulver durch eine neue variante der kopräzipitation," *Keram. Z.*, **46**(2), 85 – 88 (1994).
6. N. P. Masherova, I. B. Dubnitskaya, and V. S. Komarov, "The effect of the type of precipitator on the structure of adsorbents," *Vesti Akad. Nauk BSSR, Ser. Khim. Nauk*, No. 4, 17 – 20 (1987).
7. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Tokyo (1962).